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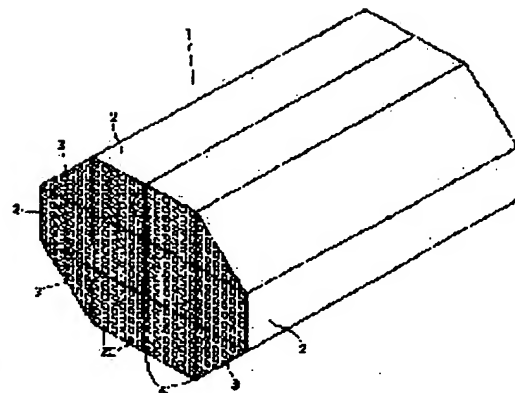
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(54) CERAMIC STRUCTURE

(57)Abstract:

PURPOSE: To improve the material characteristics, such as adhesion, of a sealant at an ordinary temperature period and a high temperature period and to improve durability of a ceramic structure.

CONSTITUTION: A plurality of through-holes formed in parallel along a longitudinal direction are formed, the end faces of the through-holes are sealed in a checkered state, and opening and closing are in a reverse relation between the input side and the output side of gas. A plurality of ceramic members 2 and 3 where the through-holes adjoining to each other are breathably intercommunicated through a porous partition wall are bounded together to form an assembly. Thus, a sealant 4 of a resilient material consisting of inorganic fibers, an inorganic binder, an organic binder, and inorganic particles and formed in such a manner that three-dimensionally crossed inorganic fibers and inorganic particles are intercoupled through an inorganic binder and an organic binder is located between the ceramic members 2 and 3 for integral adhesion.



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CLAIMS

[Claim(s)]

[Claim 1] It has two or more through tubes arranged in parallel along with a longitudinal direction. And each end face of these through tubes What closing motion has a reverse relation by the close [of gas] and appearance side, and these through tubes adjoin with *** suggestion ***** in the shape of a checker, respectively In the ceramic structure which two or more ceramic members whose aeration was mutually made possible through the porosity septum were banded, and used them as the aggregate Between said each ceramic member is consisted of an inorganic fiber, an inorganic binder, an organic binder, and an inorganic particle at least. And the ceramic structure characterized by having made the sealant of the nature material of elasticity which comes mutually to join together said inorganic fiber which is each other interwoven with in three dimensions, and an inorganic particle through an aforementioned inorganic binder and an aforementioned organic binder intervene, and pasting one.

[Claim 2] At least one or more sorts of ceramic fiber chosen from a silica alumina, a mullite, an alumina, and a silica is used for said sealant as an inorganic fiber. As an inorganic binder At least one or more sorts of colloidal sols chosen from a silica sol and alumina sol are used. As an organic binder At least one or more sorts of polysaccharide chosen from polyvinyl alcohol, methyl cellulose, ethyl cellulose, and a KARUBO methoxy cellulose is used. As an inorganic particle The ceramic structure according to claim 1 characterized by being the nature material of elasticity which comes to mix these mutually using at least one or more sorts of the inorganic powder or whiskers which are chosen from silicon carbide, silicon nitride, and boron nitride.

[Claim 3] Said sealant is the ceramic structure according to claim 2 which is solid content and is characterized by consisting of a 10 - 70wt% silica-alumina ceramic fiber, a 1 - 30wt% silica sol, a 0.1 - 5.0 wt% KARUBO methoxy cellulose, and 3 - 80wt% silicon carbide powder.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention proposes about the ceramic structure especially about the new structure

of the honeycomb structure object made from a ceramic, the monolith structure, and the other ceramic structures that arrange in parallel and come to punch two or more through tubes along with the longitudinal direction of a member.

[0002]

[Description of the Prior Art] Generally, the honeycomb structure object made from a ceramic which arranges in parallel and comes to prepare two or more through tubes along with a longitudinal direction is used as a filter for carrying out purification processing of the exhaust gas for cars, the exhaust gas from works, etc. Open-***** of a through tube [in / in this ceramic structure / that end face] presents the shape of a checker (condition which is open-***** so that adjoining through tubes may differ from others mutually). That is, a **** suggestion **** cage and the through tubes which moreover adjoin are in the Kaisei condition or the closedown condition that only one of end faces is mutually different, and these through tubes serve as checkered *****. Therefore, if one end face of one through tube is open, an other end side serves as close, and as for the through tube which adjoins this, in an other end side, an end face serves as open with close conversely [while]. And when this ceramic structure makes processed gas flow from one end face of each above-mentioned through tube, as it goes to the other end, it escapes from a porosity septum, it goes into an adjoining through tube, and makes processed gas flow out of an other end side. In addition, this ceramic structure is a porous body, and through the septum which so separates each through tube, aeration is mutually possible for it and it goes into other through tubes easily in this structure. For this, a different through tube will be circulated by the close [of gas], and appearance side. If aeration of the exhaust gas is carried out to such the ceramic structure, the particulate matter in exhaust gas (particulate) will be ****(ed) by this septum part, and the exhaust gas which flowed from one end face as mentioned above will be purified, while passing a septum and going to a tap hole. In addition, since uptake of said particulate is carried out to the septum by the side of input and it deposits especially in connection with the above-mentioned cleaning effect of this exhaust gas, blinding is started gradually and it comes to bar aeration. Therefore, the processing (only henceforth "playback") to which combustion removal of the particulate deposited on the septum which causes blinding with heating means [structure / this / ceramic] periodically, such as a burner and a heater, is carried out is needed.

[0003] However, in the above-mentioned ceramic structure, in this playback, uneven temperature distribution arise and thermal stress acts on the interior of the structure by the thermal shock which local generation of heat accompanying an uneven heating process and particulate abnormal combustion and the rapid temperature change of exhaust gas give. Consequently, the above-mentioned ceramic structure caused generating and the erosion of a crack, as a result was made to result in destruction, and had the problem of giving trouble to particulate uptake.

[0004] On the other hand, the method of reducing the thermal stress which acts on said ceramic structure is conventionally proposed as a means to solve the above-mentioned problem, by dividing for example, the ceramic structure into two or more ceramic members in respect of being parallel to a field perpendicular to the axis, or its axis (refer to JP,60-65219,A). Furthermore, the division ceramic structure which has improved the seal nature of exhaust gas is proposed by making the sealant of a non-adhesive property insert in the clearance produced between [of the ceramic structure (henceforth the "division ceramic structure") of this division form] ceramic members (refer to JP,1-63715,U).

[0005] According to each above-mentioned proposal, the division ceramic structure can open thermal stress which is seen by the ceramic structure of one apparatus by having adopted said sealant. However, since the above-mentioned sealant is a non-adhesive property, it cannot join each ceramic member firmly. Therefore, the restraint for banding a ceramic member and maintaining the gestalt as the 1 structure was required for the division ceramic structure concerning the above-mentioned conventional technique. As a means to give this restraint, a thermal-expansion nature heat insulator is conventionally prepared in the outermost periphery, or the thermal-expansion nature heat insulator is applied as an internal sealant.

[0006] However, an above-mentioned non-adhesive property sealant and an above-mentioned thermal-expansion nature heat insulator had the low endurance over the heat at the time of playback, and the repeat of vibration generated from an internal combustion engine, therefore as for the sealant, while degradation of a volumetric shrinkage or reinforcement progressed and seal nature fell, the thermal-expansion nature heat insulator also had the problem that the stability after cubical expansion declined rapidly. Therefore, the above-mentioned division ceramic structure lost the force which supports two or more ceramic members which constitute it, and with the pressure of exhaust gas, it might decompose and it might disperse. And even if it prepared the reinforcement member in the tap hole side edge side of gas, it was difficult to prevent degradation of a sealant and an improvement of endurance was desired.

[0007] What still bigger restraint is required for *****, and it becomes impossible to correspond from an early phase in the combination of the conventional non-adhesive property sealant or a thermal-expansion nature heat

insulator, and can bear the large-sized division ceramic structure especially at practical use is not obtained.

[0008] In view of such the actual condition, artificers improved the sealant which constitutes the division ceramic structure as a means for conquering previously the above-mentioned problem which the conventional technique has, and "the exhaust gas purge and its construct" using the sealant which consists of ceramic fiber, silicon carbide powder, and an inorganic binder were proposed (refer to Japanese-Patent-Application-No. No. 204242 [five to] official report). According to this proposal, since the sealant is joining two or more ceramic members mutually, the endurance of the division ceramic structure is improvable to some extent.

[0009]

[Problem(s) to be Solved by the Invention] however, the time of filling up with said sealant between ceramic members, and hardening -- migration (the phenomenon which a binder moves with desiccation removal of a solvent is said) -- a lifting -- being easy -- there was an inclination. Therefore, the sealing layer formed by hardening a sealant will become brittle. That is, the inorganic binder which constitutes the above-mentioned sealant has the operation which joins each other interwoven with point of the ceramic fiber used as an element important for the manifestation of the stress buffer function of said sealing layer which was each other interwoven with in three dimensions while joining a ceramic member and a sealing layer firmly. However, since this inorganic binder moved to a plane of composition with a ceramic member from the interior of a sealing layer by the migration which happens in process of desiccation hardening, and the junction force of said each other interwoven with point declined, as a result the fall of the ceramic structure itself on the strength was caused, desired endurance was not able to be satisfied. Moreover, the silicon carbide powder which constitutes the above-mentioned sealant moved in connection with the above-mentioned migration similarly, and a fall and ununiformity of thermal conductivity were caused, as a result it became the cause of a regeneration efficiency fall of the ceramic structure.

[0010] On the other hand, the method of improving the endurance of the structure is also considered by controlling the above-mentioned migration. However, in order that desiccation hardening of a sealant may take long duration to this approach and it may worsen productivity, it is not desirable. As explained above, as for the above-mentioned conventional division ceramic structure, the room of an improvement was still left behind about the endurance as the ceramic structure etc.

[0011] This invention is made in order to solve the problem of the versatility mentioned above which the conventional technique has, and that main purpose is in raising the endurance of the ceramic structure.

[0012] Other purposes of this invention are to improve the material properties of the sealant at the time of ordinary temperature and an elevated temperature, such as an adhesive property.

[0013] The purpose of further others of this invention is by improving the adhesive property and thermal conductivity of a sealant at the time of ordinary temperature and an elevated temperature to raise both the endurance of the division ceramic structure, and regeneration efficiency to coincidence, maintaining elasticity and thermal resistance.

[0014]

[Means for Solving the Problem] As a result of artificers' continuing research wholeheartedly towards implementation of the above-mentioned purpose, invention which considers the contents shown below as a summary configuration was found out. This invention has two or more through tubes arranged in parallel along with a longitudinal direction. Namely, and each end face of these through tubes What closing motion has a reverse relation by the close [of gas] and appearance side, and these through tubes adjoin with **** suggestion ***** in the shape of a checker, respectively In the ceramic structure which two or more ceramic members whose aeration was mutually made possible through the porosity septum were banded, and used them as the aggregate Between said each ceramic member is consisted of an inorganic fiber, an inorganic binder, an organic binder, and an inorganic particle at least. And it is the ceramic structure characterized by having made the sealant of the nature material of elasticity which comes mutually to join together said inorganic fiber which is each other interwoven with in three dimensions, and an inorganic particle through an aforementioned inorganic binder and an aforementioned organic binder intervene, and pasting one.

[0015] At least one or more sorts of ceramic fiber chosen from a silica alumina, a mullite, an alumina, and a silica is used for said sealant as an inorganic fiber here. As an inorganic binder At least one or more sorts of colloidal sols chosen from a silica sol and alumina sol are used. An organic binder uses at least one or more sorts of polysaccharide chosen from polyvinyl alcohol, methyl cellulose, ethyl cellulose, and a KARUBO methoxy cellulose. As an inorganic particle It is desirable that it is a nature material of elasticity using at least one or more sorts of the inorganic powder or whiskers which are chosen from silicon carbide, silicon nitride, and boron nitride.

[0016] As for the above-mentioned sealant, specifically, it is more desirable to have the configuration described below.

** . -- the content of the silica-alumina ceramic fiber among ceramic fiber -- solid content -- it is -- 10 -

70wt% -- it is preferably desirable that it is 20 - 30wt% more preferably 10 - 40wt%. This reason is because the effectiveness as an elastic body falls while causing decline in thermal conductivity, if the effectiveness as an elastic body falls less than [10wt%] and a content exceeds 70wt% on the other hand.

[0017] **. -- the content of the silica sol among colloidal sols -- solid content -- it is -- 1 - 30wt% -- it is preferably desirable that it is 5 - 9wt% more preferably 1 - 15wt%. This reason is that it will cause decline in thermal conductivity if a content causes the fall of bond strength less than [1wt%] and exceeds 30wt% on the other hand.

[0018] **. -- the content of the carboxymethyl cellulose among polysaccharide -- solid content -- it is -- 0.1 - 5.0 wt% -- desirable -- It is desirable that it is 0.4 - 0.6 wt% more preferably 0.2 - 1.0 wt%. This reason is that an organic binder will be burned down by the hot heat history, and reinforcement will fall if a content cannot control migration less than [0.1 wt%] but exceeds 5.0 wt% on the other hand.

[0019] **. -- the content of the silicon carbide powder among inorganic powder or a whisker -- solid content -- it is -- 3 - 80wt% -- it is preferably desirable that it is 20 - 40wt% more preferably 10 - 60wt%. This reason is that it will cause the fall of the bond strength in the time of an elevated temperature if a content causes decline in thermal conductivity and exceeds 80wt% on the other hand less than [3wt%].

[0020] **. -- the silica-alumina ceramic fiber among the ceramic fiber which constitutes the above-mentioned sealant -- the shot content -- 1 - 10wt% -- 1 - 5wt%, it is 1 - 3wt% more preferably, and it is preferably desirable for fiber length to be 1-20mm more preferably 1-50mm one to 100 mm. This reason is that it will damage the wall of a sealant-ed (ceramic member) if a manufacture top is difficult for making a shot content into less than [1wt%] and a shot content exceeds 50wt(s)%. on the other hand, fiber length cannot form the elastic structure in less than 1mm -- it is because it becomes like fluff and distribution of a non-subtlety particle can make thickness of a sealant thin neither of if the worst happens, so the thermally conductive fall between sealants-ed will be caused if 100 mm is exceeded.

[0021] **. For the silicon carbide powder among the inorganic powder which constitutes the above-mentioned sealant, or a whisker, the particle size is 0.01-100. It is preferably desirable mum and that it is 0.1-10 micrometers more preferably 0.1-15 micrometers. Particle size this reason It is because adhesive strength (reinforcement) and a thermally conductive fall will be caused and it will become cost quantity by less than 0.01 micrometers on the other hand, if it exceeds 100 micrometers.

[0022]

[Function] The description of the ceramic structure concerning this invention is in the configuration of the sealant which joins two or more ceramic members to one, and can band together. First, when the inorganic fiber and the organic binder which constitute [1st] a sealant become entangled mutually, the homogeneity of an organization and the junction nature in a low-temperature field are improved, and, specifically, it is in the point which raised the endurance of the ceramic structure. That is, by adopting the organic binder which carries out desiccation hardening at an early stage, generating of migration which is seen by the conventional sealant is controlled, and the description is that it enabled maintenance of three-dimensions-association of inorganic fibers, and immobilization of the inorganic particle to an inorganic fiber. Even if the ceramic structure which was systematically uniform, could use the sealant as nature material of elasticity which is excellent in an adhesive property, elasticity, and reinforcement by this, consequently banded two or more ceramic members together to one by such sealant does not give the restraint from the outside, it has sufficient bond strength, and it can open thermal stress to coincidence.

[0023] The 2nd description is the effectiveness of a tangle to the inorganic fiber and the inorganic binder which constitute a sealant, and is in the point that the bond strength in an elevated-temperature field is maintainable. It is thought that this ceramics exists in each other interwoven with point of inorganic fibers by ceramic-izing an inorganic binder by heating, and that reason contributes an organic binder to junction to inorganic fibers and a ceramic member in an elevated-temperature field although baking removal will be carried out. On the other hand, this inorganic binder can hold bond strength also in a low-temperature field with desiccation and heating.

[0024] Therefore, it can consider as the ceramic structure which is excellent in the bond strength in a low-temperature region and a pyrosphere according to ceramic fiber, such as a silica alumina, the above-mentioned effectiveness by tangle of inorganic binders, such as a silica sol, and the synergistic effect with said organic binder.

[0025] An inorganic particle is placed between the front face of an inorganic fiber, the front face of an inorganic binder, and the interior, and the 3rd description is in the point of improving the thermal conductivity of the ceramic structure. Especially the inorganic particle of a nitride or carbide can raise thermal conductivity remarkably with the high temperature conduction property which a nitride or carbide has.

[0026] Therefore, the sealant containing the above-mentioned inorganic particle can prevent breakage of the ceramic structure effectively, without causing a temperature peak phenomenon at the time of playback at the

same time it will fill the opening made when two or more ceramic members are combined, if it excels in thermal conductivity, for example, uses for the filter for exhaust gas purges. And generating of the crack by the heat cycle is reduced, and heating of the edge section of a filter periphery can also be performed comparatively in a short time, and can raise regeneration efficiency.

[0027] Hereafter, the ceramic structure of this invention is explained to a detail. The ceramic structure needs to equip with elasticity, thermal conductivity, junction nature, reinforcement, etc. the sealant which constitutes it other than thermal resistance, when using as a filter for exhaust gas purges. If excelled in elasticity, even when thermal stress will join a filter with heating, it is because the thermal stress can be opened certainly. Moreover, it is because the heat of a heating element will conduct that there is no nonuniformity in the whole structure promptly and the temperature gradient inside an exhaust gas purge will also become small, if excelled in thermal conductivity. Moreover, it is because it will become what is excellent in the adhesive property of the ceramic members which have banded together adjacently, and is excellent also in the endurance of the ceramic structure itself if excelled in junction nature and reinforcement.

[0028] This invention is characterized by having joined together mutually through an aforementioned inorganic binder and an aforementioned organic binder, and making into the elastic structure said inorganic fiber and inorganic particle which are each other interwoven with in three dimensions, using an inorganic fiber, an inorganic binder, an organic binder, and an inorganic particle as a configuration of the sealant which shows the above-mentioned physical properties.

[0029] Here, as an inorganic fiber, although there are silica-alumina ceramic fiber, a mullite fiber, an alumina fiber, and a silica fiber, while silica-alumina ceramic fiber is desirable and excelling in elasticity, the operation which absorbs thermal stress is shown especially.

[0030] A colloidal sol is desirable, for example, as an inorganic binder, although there are alumina sol and a silica sol, especially a silica sol is desirable, and it acts as adhesives (inorganic binder). It is easy to receive and this silica sol is SiO₂ easily by baking. Since it becomes, it is suitable as adhesives in an elevated-temperature field, and moreover, it excels in insulation.

[0031] As an organic binder, a hydrophilic organic macromolecule is desirable and especially polysaccharide is more desirable. Although there are polyvinyl alcohol, methyl cellulose and ethyl cellulose, a carboxymethyl cellulose, etc., especially a carboxymethyl cellulose is desirable, the fluidity at the time of assembly is secured (contributing to the improvement in workability), and, specifically, the outstanding adhesive property in an ordinary temperature field is shown.

[0032] As an inorganic particle, the inorganic particle of carbide and/or a nitride is desirable, for example, there are silicon carbide, silicon nitride, and boron nitride. These carbide and nitrides are very large, and the heat conductivity is placed between a ceramic fiber front face, the front face of a colloidal sol, and the interior, and contributes them to thermally conductive improvement. For example, the thermal conductivity of silicon carbide is thermal conductivity of 0.19 cal/cm-sec and **, and boron nitride. To 0.136 cal/cm-sec and **, and this, the thermal conductivity of an alumina is 0.08 cal/cm-sec and ** extent, and it turns out that especially carbide and a nitride are effective for an improvement of thermal conductivity. Especially silicon carbide is the optimal in respect of heat conduction among the inorganic particles of these carbide and a nitride. Boron nitride is because concordance with ceramic fiber is lower than silicon carbide. That is, it is the reason that silicon carbide has all of an adhesive property, thermal resistance, a water resisting property, and thermal conductivity.

[0033]

[Example] Below, the example which materialized the ceramic structure of this invention in the filter for exhaust gas purges attached by the diesel power plant is explained in detail based on drawing 1 - drawing 5. Drawing 1 is drawing showing the filter 1 for exhaust gas purges which used the ceramic structure of this invention, and drawing 2 is the partial cross-section enlarged drawing of this filter. In these drawings, the filter 1 for exhaust gas purges makes the sealant (1.5-3.0mm in thickness) 4 which becomes between members from the nature material of elasticity about eight prismatic form ceramic members 2 and the ceramic member 3 of the shape of four cross-section rectangular equilateral triangle intervene, and one is pasted and it is constituted. Drawing 3 - 5 are drawing showing the ceramic member 2 which constitutes some filters 1 for exhaust gas purges. In these drawings, cross-section abbreviation square-like through tube 2a is regularly drilled by the prismatic form (33mmx33mmx150mm) ceramic member 2 along the direction of an axis. Such through tube 2a is 0.3mm in thickness. It is mutually separated with porosity septum 2b. The closure of the end of either the exhaust gas inflow side of each through tube 2a or an outflow side is carried out to the shape of a checker by piece of the closure 2c made from a porosity sintered compact. Consequently, it is in the condition that the cels C1 and C2 which carry out opening to either the inflow side of the ceramic member 2 or an outflow side were formed. In addition, to septum 2b of cels C1 and C2, the oxidation catalyst which consists of platinum group metals, other metallic elements, its oxide, etc. may be supported. When it supports, it is for particulate ignition temperature to

fall. Moreover, the ceramic member 3 has the same configuration as the ceramic member 2 except for a cross-section configuration being a rectangular equilateral triangle-like. And in the case of the ceramic members 2 and 3 which constitute the filter 1 for exhaust gas purges of this example, for the thickness of 43% and a cell wall, 0.3mm and a cell pitch are [an average pore diameter / 10 micrometers and porosity] 1.8mm. It is set up. This example produces the filter 1 for exhaust gas purges in a configuration which was explained above, and performs the performance evaluation of the filter.

[0034] (Example 1)

(1) Wet blending of 51.5 % of the weight of alpha mold silicon carbide powder and the 22 % of the weight of the beta mold silicon carbide powder was carried out, and into the obtained mixture, 6.5% of the weight, an organic binder (methyl cellulose) and water were added by a unit of 20% of the weight, and were kneaded, respectively. Next, the honeycomb-like generation form was acquired for a plasticizer and lubricant small quantity, in addition by kneading further and carrying out extrusion molding of this kneading object.

(2) Next, after drying using the dryer according this generation form to microwave and closing through tube 2a of a Plastic solid after that with the paste for the piece of the closure 2c formation made from a porosity sintered compact, the paste for piece of the closure 2c was again dried using the dryer. And after degreasing this desiccation object by 400 **, it was further calcinated at 2200 degrees C under argon atmosphere, and the ceramic honeycomb-like members 2 and 3 were obtained by porosity.

(3) 23.3 % of the weight (it is 0.1 – 100 mm in alumina silicate ceramic fiber, 3% of shot content, and fiber length) of ceramic fiber, and mean diameter 0.3 30.2 % of the weight of silicon carbide powder of mum, 7 % of the weight (the amount of conversions of SiO₂ of a sol is 30%) of silica sols as an inorganic binder, carboxymethyl cellulose as an organic binder 0.5 % of the weight and 39 % of the weight of water were mixed, what was kneaded was made into the shape of a paste, and the sealant was created.

(4) It was filled up with said sealant the ceramic member 2 and between three, it dried and hardened in 50 – 100 **x 1 hour, and the filter 1 which joined the ceramic members 2 and 3 and a sealant 4, and was unified as shown in drawing 1 R > 1 was produced.

In addition, without causing migration, it was able to dry and the above-mentioned sealant was able to be hardened.

[0035] (Example 2) Although this example was the same as that of an example 1 fundamentally, it replaced the sealant with the thing in an example 1, and was taken as the following. 25 % of the weight (it is 0.1 – 100 mm in a mullite fiber and 5% fiber length of shot content) of ceramic fiber, and mean diameter 1.0 30 % of the weight of silicon nitride powder of mum, 7 % of the weight (the amount of conversions of alumina sol is 20%) of alumina sols as an inorganic binder, and polyvinyl alcohol 0.5 as an organic binder Weight % and 37.5 % of the weight of alcohol were mixed, and what was kneaded was used. In addition, without causing migration, it was able to dry and the above-mentioned sealant was able to be hardened.

[0036] (Example 3) Although this example was the same as that of an example 1 fundamentally, it replaced the sealant with the thing in an example 1, and was taken as the following. 8 % of the weight (the amount of conversions of alumina sol is 20%) of alumina sols as 23 % of the weight (it is 0.1 – 100 mm in an alumina fiber and 4% fiber length of shot content) of ceramic fiber, 35 % of the weight of boron nitride powder of 1 micrometer of mean diameters, and an inorganic binder, and ethyl cellulose 0.5 as an organic binder Weight % and 35.5 % of the weight of acetones were mixed, and what was kneaded was used. In addition, without causing migration, it was able to dry and the above-mentioned sealant was able to be hardened.

[0037] (Example 1 of a comparison) Although this example was the same as that of an example 1 fundamentally, it replaced the sealant with the thing in an example 1, considered as the following which is the conventional sealant, and, finally covered the outermost periphery of a filter 1 with the heat insulator (63 % of the weight of ceramic fiber, 7 % of the weight of alpha-sepiolites, 20 % of the weight of non-expanded vermiculites, 10 % of the weight of organic binders) of ceramic fiber further. 13.3 % of the weight of silica sols and 42.5 % of the weight of water as 44.2 % of the weight (it is 30 – 100 mm in alumina-silica fiber and shot content 2.7 % and fiber length) of ceramic fiber and an inorganic binder were mixed, and it was used by making into the shape of the shape of a paste, and a sheet what was kneaded. In addition, when drying and hardening the above-mentioned sealant, it caused migration.

[0038] It carried out by the approach of showing below the performance evaluation of the filter 1 produced in examples 1–3 and the example 1 of a comparison.

(Measurement of the bond strength after the first stage and a thermo cycle) As shown in drawing 6 , from the filter 1, three ceramic members were started as a test piece, the load was applied to the main ceramic member, and the load when peeling arises was measured. Moreover, since the rapid heating from ordinary temperature to 900 ** and quenching were expected, actual use estimated what performed the thermo cycle test which is room temperature – 900 degree C. The measurement result of the bond strength after the ceramic member 2 which

constitutes a filter 1, the early stages of between three, and a thermo cycle (100 after a time) was shown in Table 1.

[0039]

[Table 1]

	初期状態の接着強度	ヒートサイクル後の接着強度
実施例 1	4.6 kg/cm ²	7.6 kg/cm ²
実施例 2	4.5 kg/cm ²	5.3 kg/cm ²
実施例 3	4.3 kg/cm ²	5.6 kg/cm ²
比較例 1	2.3 kg/cm ²	0.76 kg/cm ²

In addition, it is presumed that the reason the direction of reinforcement after a thermo cycle improves is for a sintering operation of the silica by heating of 900 **.

[0040] (Measurement of thermal conductivity) As shown in drawing 7, four ceramic members are started as a test piece, a periphery is enclosed with a heat insulator, and it installs on a heater 6, and heats for 20 minutes. The temperature gradient of T1 and T2 at this time was measured. The result of having measured the temperature gradient of T1 and T2 shown in drawing 7 about each examples 1-3 and the example of a comparison was shown in Table 2.

[0041]

[Table 2]

	T 1 - T 2 温度差
実施例 1	5 5 ℃
実施例 2	6 5 ℃
実施例 3	7 0 ℃
比較例 1	1 8 0 ℃

[0042] Since the filter using the ceramic structure of this invention has very high bond strength and was excellent also in the heat cycle property with an elevated temperature and ordinary temperature, it checked excelling in the endurance as a filter, so that clearly from the above result. And this ceramic structure can reduce generating of the peak temperature in the ceramic member located in the interior of a filter, and since the heating up time of the ceramic structure located in an edge part can be shortened, it can make coincidence realize improvement in regeneration efficiency, since it excels also in thermal conductivity.

[0043] In addition, it is not limited to a thing given in the above-mentioned example, and the configuration of the filter 1 with which the ceramic structure of this invention is applied can be changed into the following configurations. For example, the number of combination of (a) ceramic member may not be 12 pieces like said example, and it is possible to make it the number of arbitration. In this case, of course, it is also possible to use it, combining different ceramic members, such as size and a configuration, suitably. In addition, it is advantageous to take the configuration which combined two or more ceramic members, especially when producing the large-sized filter for exhaust gas purges.

(b) The filter 1 of said example can be caught even if one big filter will be divided into plurality along the direction of an axis so to speak. The modification of changing into the condition which divided the filter in the shape of a doughnut, the condition of having divided at right angles to the direction of an axis, etc. there is also considered.

(c), of course, it is possible for it not to be restricted only to the ceramic members 2 and 3 of the shape of a honeycomb as shown in said example, for example, to adopt the shape of the shape of the shape of a three-

dimensional network and form and a noodle and a fiber etc. Moreover, as the ceramic member 2 and an ingredient for three, even if it chooses things other than silicon carbide, it is easy to be natural.

(d) When it constitutes a filter 1, it is good also as a configuration which comes to prepare a heater the ceramic member 2 and between three. In this case, it is not limited only to a heater being a metal wire. That is, a heater may be produced by approaches, such as printing of metal metallizing and conductive paste, and sputtering.

[0044] In this example, although the example materialized in the filter for exhaust gas purges in which the ceramic structure of this invention is attached by the diesel power plant was explained, this ceramic structure can be used as a barrier filter of for example, the member for heat exchangers or a high-temperature fluid, and an elevated-temperature steam besides the filter for exhaust gas purges.

[0045]

[Effect of the Invention] Since the ceramic structure of this invention is excellent in bond strength regardless of temperature as explained above, and it moreover excels also in thermal conductivity, if it applies to the filter for exhaust gas purges, compaction of playback time amount and improvement in regeneration efficiency or endurance are realizable, for example.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the perspective view showing the filter for exhaust gas purges using the ceramic structure of this invention.

[Drawing 2] It is the partial expanded sectional view of the filter for exhaust gas purges using the ceramic structure of this invention.

[Drawing 3] It is the perspective view showing the ceramic member of the filter for exhaust gas purges concerning this invention.

[Drawing 4] it can set on the A-A line of drawing 3 -- it is a fracture expanded sectional view a part.

[Drawing 5] It is an expanded sectional view in the B-B line of drawing 4 .

[Drawing 6] It is the explanatory view of a measurement trial of bond strength.

[Drawing 7] It is the explanatory view of a measurement trial of thermal conductivity.

[Description of Notations]

- 1 Filter for Exhaust Gas Purges
- 2 Three Ceramic member
- 4 Sealant
- 5 Heat Insulator

[Translation done.]

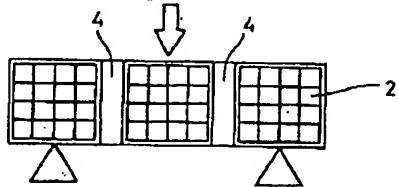
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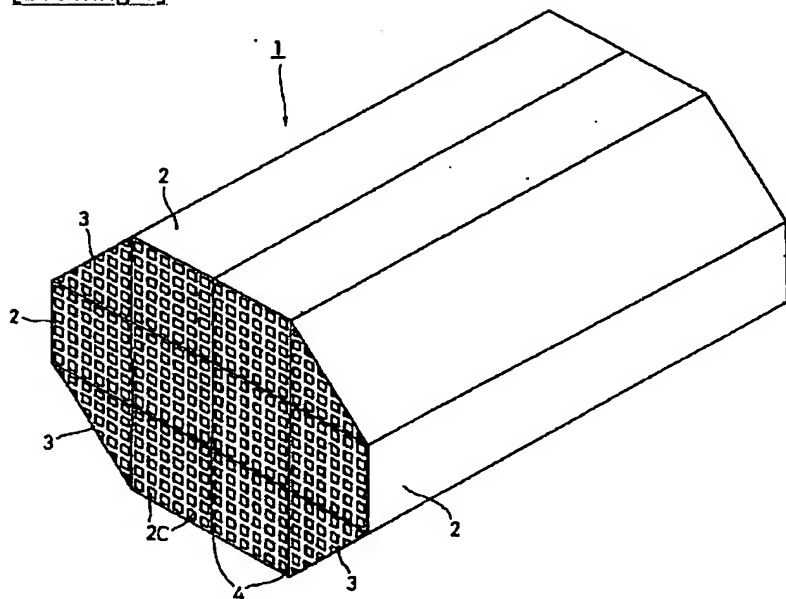
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DRAWINGS

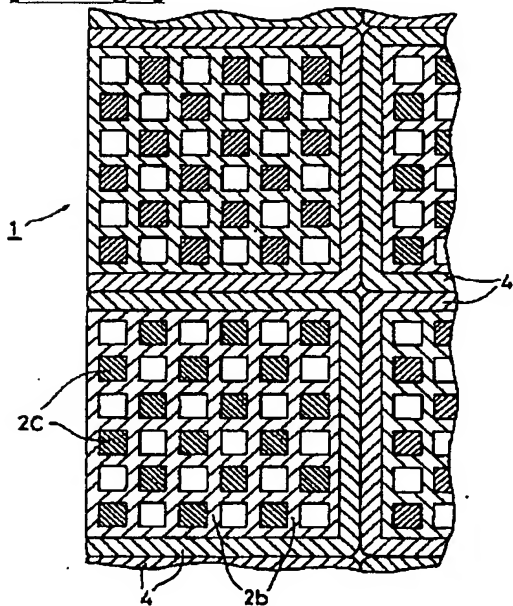
[Drawing 6]



[Drawing 1]

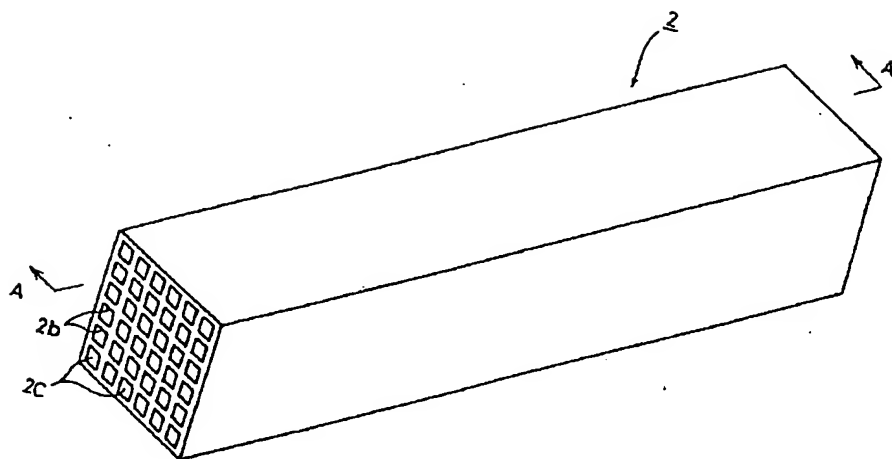


[Drawing 2]

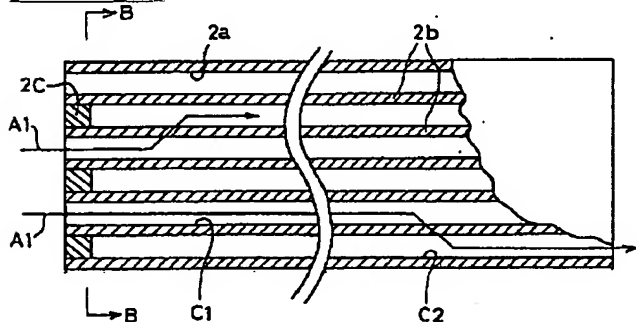


[Drawing 3]

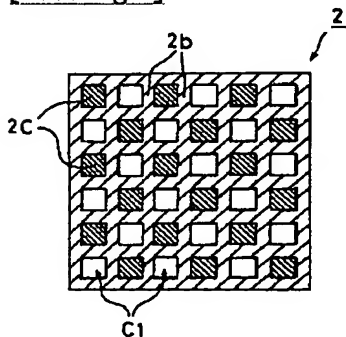
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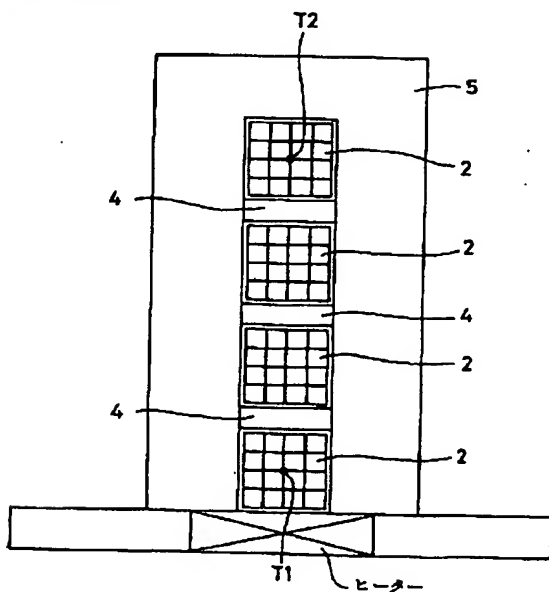
[Drawing 4]



[Drawing 5]



[Drawing 7]



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[Translation done.]

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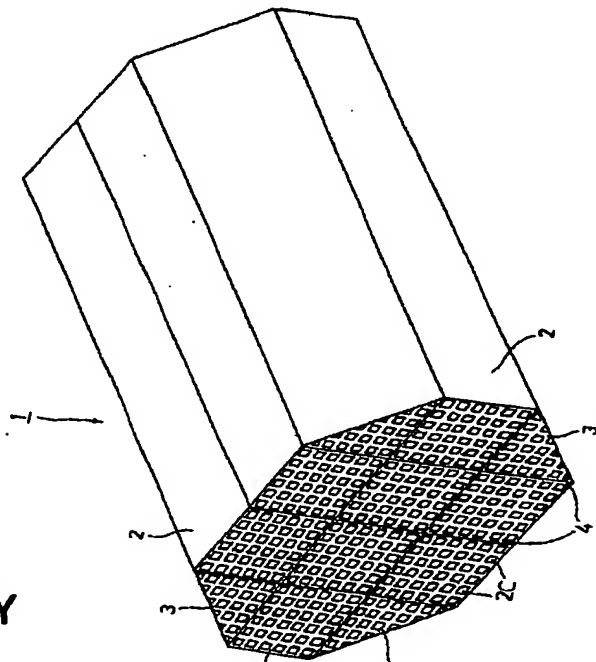
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(54) 【発明の名称】 セラミック構造体

(57) 【要約】

【目的】 常温時および高温時におけるシール材の接着性等の材料特性を改善し、セラミック構造体の耐久性を向上させること。

【構成】 長手方向に沿って並列する複数の貫通孔を有し、かつ、これらの貫通孔の各端面は、それぞれ市松模様状に目封じされていると共に、ガスの入側と出側とで接するものどうしは、多孔質な隔壁を通じて互いに通気可能にしたセラミック部材2、3を、複数個結束させて集合体としたセラミック構造体において、前記各セラミック部材2、3の相互間を、少なくとも無機繊維、無機バインダー、有機バインダーおよび無機粒子からなり、かつ三次元的に交錯する前記無機繊維と無機粒子とを、前記の無機バインダーおよび有機バインダーを介して互いに結合してなる弾性質素材のシール材4を介在させて、一体に接着したことを特徴とするセラミック構造体である。



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を維持するための拘束力が必要であった。この拘束力を付与する手段として、従来、熱膨張性断熱材を最外周部に設けたり、あるいは熱膨張性断熱材を内部シール材として適用している。

【0006】しかしながら、上記の非接着性シール材や熱膨張性断熱材は、再生時の熱や、内燃機関から発生する振動の繰り返しに対する耐久性が低く、そのために、シール材は、体積収縮や強度の劣化が進みシール性が低下してしまう一方、熱膨張性断熱材も、体積膨張後の復元力が急激に低下するという問題があった。従って、上記分割セラミック構造体は、それを構成する複数のセラミック部材を支持する力を失い、排気ガスの圧力により分解、飛散してしまうことがあった。しかも、たとえガスの流出口側端面に補強部材を設けてもシール材の劣化を防止することは難しく、耐久性の改善が望まれていた。

【0007】とくに、大型の分割セラミック構造体を形成するには、さらに大きな拘束力が必要であり、従来の非接着性シール材や熱膨張性断熱材の組合せでは、初期の段階から対応できなくなり、実用に耐え得るものが得られていない。

【0008】このような実情に鑑み、発明者らは、先に、従来技術が抱える上記問題を克服するための手段として、分割セラミック構造体を構成するシール材を改良し、セラミックファイバー、炭化珪素粉末および無機バインダーとからなるシール材を用いた「排気ガス浄化装置およびその構成体」を提案した（特願平5-204242号公報参照）。この提案によれば、シール材が複数のセラミック部材を相互に接合させているので、分割セラミック構造体の耐久性をある程度改善することができる。

【0009】【発明が解決しようとする課題】しかしながら、前記シール材は、セラミック部材相互間に充填され硬化する際に、マイグレーション（溶媒の乾燥除去に伴ってバインダーが移動する現象をいう）を起こし易い傾向があった。そのため、シール材を硬化することにより形成されるシール層が脆弱なものとなる。つまり、上記シール材を構成する無機バインダーは、セラミック部材とシール層とを、強固に接合するとともに、前記シール層の応力緩衝機能の発現に重要な要素となる三次元的に交錯したセラミックファイバーの交錯点を接合する作用がある。ところが、この無機バインダーは、乾燥硬化の過程で起こるマイグレーションによってシール層内部からセラミック部材との接合面に移動し、前記交錯点の接合力が低下して、ひいてはセラミック構造体自体の強度低下を招くので、所望の耐久性を満足させることができなかった。また、上記シール材を構成する炭化珪素粉末も同様に上記マイグレーションに伴って移動し、熱伝導率の低下や不均一を招き、ひいてはセラミック構造体の再生効率低下の原因となった。

【0010】これに対して、上記マイグレーションを抑制することによって、構造体の耐久性を改善する方法が考えられる。しかし、この方法は、シール材の乾燥時に長時間を要して生産性を悪くするため好ましくない。以上説明したように、上記従来の分割セラミック構造体は、セラミック構造体としての耐久性等に関し、依然として改善の余地が残されていた。

【0011】この発明は、従来技術が抱えている上述した種々の問題を解消するためになされたものであり、その主たる目的は、セラミック構造体の耐久性を向上させることにある。

【0012】この発明の他の目的は、常温時および高温時におけるシール材の接着性等の材料特性を改善することにある。

【0013】この発明のさらに他の目的は、弾性と耐熱性を維持しつつ、常温時および高温時におけるシール材の接着性ならびに熱伝導性を改善することにより、分割セラミック構造体の耐久性と再生効率の両方を同時に向上させることにある。

【0014】

【課題を解決するための手段】上記目的の実現に向け、発明者らは鋭意研究を続けた結果、以下に示す内容を要旨構成とする発明を見出した。すなわち、この発明は、長手方向に沿って並列する複数の貫通孔を有し、かつ、これらの貫通孔の各端面は、それぞれ市松模様状に目封じされていると共に、ガスの入側と出側とでは開閉が逆の関係にあり、そして、これらの貫通孔の隣接するものどうしは、多孔質な隔壁を通じて互いに通気可能にしたセラミック部材を、複数の結束させて集合体としたセラミック構造体において、前記各セラミック部材の相互間を、少なくとも無機繊維、無機バインダー、有機バインダーおよび無機粒子からなり、かつ三次元的に交錯する前記無機繊維と無機粒子とを、前記の無機バインダーおよび有機バインダーを介して互いに結合してなる弾性質素材のシール材を介させて、一体に接着したことを特徴とするセラミック構造体である。

【0015】ここで、前記シール材は、無機繊維とし、シリカーアルミナ、ムライト、アルミナおよびシリカから選ばれる少なくとも1種以上のセラミックファイバーを用い、無機バインダーとして、シリカゾルおよびアルミナゾルから選ばれる少なくとも1種以上のコロイドゾルを用い、有機バインダーが、ポリビニルアルコール、メチルセルロース、エチルセルロースおよびカルボメトキシセルロースから選ばれる少なくとも1種以上の多糖類を用い、そして無機粒子として、炭化珪素、窒化珪素および窒化硼素から選ばれる少なくとも1種以上の無機粉末またはウイスキーを用いた弾性質素材であることが望ましい。

【0016】具体的には、上記ミ...

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うなときでも、その熱応力を確実に開放することができるからである。また、熱伝導性に優れていると、発熱体の熱が構造体全体に速やかにかつムラなく伝導し、排気ガス浄化装置内部の温度差も小さくなるからである。また、接合性および強度に優れたものであると、隣接して結束されているセラミック部材同士の接着性が優れ、セラミック構造体自体の耐久性も優れるものとなるからである。

【0028】この発明は、上記物性を示すシール材の構成として、無機繊維、無機バインダー、有機バインダーおよび無機粒子を用い、かつ、三次元的に交錯する前記無機繊維と無機粒子とを、前記の無機バインダーおよび有機バインダーを介して互いに結合して弾性構造体としたことを特徴とする。

【0029】ここで、無機繊維としては、シリカーアルミナセラミックファイバー、ムライトファイバー、アルミナファイバーおよびシリカファイバーがあるが、特にシリカーアルミナセラミックファイバーが望ましく、弾性に優れると共に熱応力を吸収する作用を示す。

【0030】無機バインダーとしては、コロイダルゾルが望ましく、例えば、アルミナゾル、シリカゾルがあるが、特にシリカゾルが望ましく、接着剤（無機バインダー）として作用する。このシリカゾルは、入手しやすく、焼成により容易に SiO_2 となるため高温領域での接着剤として好適であり、しかも、絶縁性に優れている。

【0031】有機バインダーとしては、親水性有機高分子が望ましく、特に多糖類がより好ましい。具体的には、ポリビニルアルコールやメチルセルロース、エチルセルロース、カルボキシメチルセルロースなどがあるが、特にカルボキシメチルセルロースが望ましく、組立時の流動性を確保し（作業性向上に寄与し）、常温領域での優れた接着性を示す。

【0032】無機粒子としては、炭化物および/または窒化物の無機粒子が望ましく、例えば炭化珪素、窒化珪素および窒化硼素がある。これらの炭化物や窒化物は、熱伝導率が非常に大きく、セラミックファイバー表面やコロイダルゾルの表面および内部に介在して熱伝導性の向上に寄与する。例えば、炭化珪素の熱伝導率は $0.19 \text{ cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}$ 、窒化硼素の熱伝導率は $0.136 \text{ cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}$ 、これに対してアルミナの熱伝導率は $0.08 \text{ cal/cm} \cdot \text{sec} \cdot ^\circ\text{C}$ 程度であり、特に炭化物や窒化物は、熱伝導率の改善に効果的であることが判る。これらの炭化物および窒化物の無機粒子のうち、特に炭化珪素は熱伝導の点で最適である。窒化硼素は、セラミックファイバーとのなじみが炭化珪素より低いからである。すなわち、接着性、耐熱性、耐水性および熱伝導率を総て兼ね備えているのが炭化珪素であることがその理由である。

【0033】

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【実施例】以下に、この発明のセラミック構造体をディーゼルエンジンに取り付けられる排気ガス浄化装置用フィルタに具体化した実施例を図1～図5に基づき詳しく説明する。図1は、この発明のセラミック構造体を用いた排気ガス浄化装置用フィルタ1を示す図であり、図2は、このフィルタの部分断面拡大図である。これらの図において、排気ガス浄化装置用フィルタ1は、8本の角柱状のセラミック部材2と4本の断面直角二等辺三角形状のセラミック部材3を、部材相互間に弾性質素材からなるシール材（厚さ $1.5 \sim 3.0 \text{ mm}$ ）4を介在させて一体に接着して構成されている。図3～5は、排気ガス浄化装置用フィルタ1の一部分を構成しているセラミック部材2を示す図である。これらの図において、角柱状（ $33 \text{ mm} \times 33 \text{ mm} \times 150 \text{ mm}$ ）のセラミック部材2には、断面略正方形の貫通孔2aがその軸線方向に沿って規則的に穿設されている。これらの貫通孔2aは、厚さ 0.3 mm の多孔質な隔壁2bによって互いに隔てられている。各貫通孔2aの排気ガス流入側または流出側のいずれかの一端は、多孔質焼結体製の封止片2cによって市松模様状に封止されている。その結果、セラミック部材2の流入側または流出側のいずれか一方のみに開口するセルC1、C2が形成された状態となっている。なお、セルC1、C2の隔壁2bには、白金族元素やその他の金属元素およびその酸化物等からなる酸化触媒を担持してもよい。担持するとバディキュレートの着火温度が低下するためである。また、セラミック部材3は、断面形状が直角二等辺三角形状であることを除いてセラミック部材2と同様の構成を有している。そして、本実施例の排気ガス浄化装置用フィルタ1を構成するセラミック部材2、3の場合、平均気孔径が $10 \mu\text{m}$ 、気孔率が43%、セル壁の厚さが 0.3 mm 、セルピッチが 1.8 mm に設定されている。本実施例は、以上説明したような構成にある排気ガス浄化装置用フィルタ1を作製して、そのフィルタの性能評価を行ったものである。

【0034】（実施例1）

(1) α 型炭化珪素粉末51.5重量%と β 型炭化珪素粉末22重量%とを湿式混合し、得られた混合物に有機バインダー（メチルセルロース）と水とをそれぞれ6.5重量%、20重量%ずつ加えて混練した。次に、可塑剤と潤滑剤を少量加えてさらに混練し、この混練物を押出成形することにより、ハニカム状の生成形体を得た。

(2) 次に、この生成形体をマイクロ波による乾燥機を用いて乾燥し、その後、成形体の貫通孔2aを多孔質焼結体製の封止片2c形成用のペーストによって封止した後、再び乾燥機を用いて封止片2c用ペーストを乾燥させた。そして、この乾燥体を 400°C で脱脂した後、更にそれをアルゴン雰囲気下にて 2200°C で焼成し、多孔質でハニカム状のセラミック部材2、3を得た。

(3) セラミックファイバー（アルミナシリケートセラミックファイバー、ショット含有率3%、繊維長さ $0.1 \sim$

	T1-T2温度差
実施例1	55℃
実施例2	65℃
実施例3	70℃
比較例1	180℃

【0042】以上の結果から明らかなように、この発明のセラミック構造体を用いたフィルタは、高温、常温でも非常に高い接着強度を有し、熱サイクル特性にも優れることから、フィルタとしての耐久性に優れることを確認した。しかも、このセラミック構造体は、熱伝導性にも優れるので、フィルタ内部に位置するセラミック部材でのピーク温度の発生を低減でき、エッジ部分に位置するセラミック構造体の昇温時間を短縮させることができることから、再生効率の向上を同時に実現させることができる。

【0043】なお、この発明のセラミック構造体が適用されるフィルタ1の構成は、上記実施例に記載のものに限定されることはなく、以下のような構成に変更することが可能である。例えば、

(a) セラミック部材の組み合わせ数は前記実施例のように12個でなくても良く、任意の数にすることが可能である。この場合、サイズ・形状等の異なるセラミック部材を適宜組み合わせ使用することも勿論可能である。なお、セラミック部材を複数個組み合わせた構成を採るときは、大型の排気ガス浄化装置用フィルタを作製するときに特に有利である。

(b) 前記実施例のフィルタ1は、いわば1つの大きなフィルタが軸線方向に沿って複数個に分割された状態になっているとも捉えることができる。そこで、例えばフィルタをドーナツ状に分割した状態、軸線方向に垂直に分割した状態などにするというような変形例も考えられる。

(c) 前記実施例にて示したようなハニカム状のセラミック部材2、3のみに限られず、例えば三次元網目構造、フォーム状、ヌードル状、ファイバー状等を採用す

ることが勿論可能である。また、セラミック部材2、3用の材料として、炭化珪素以外のものを選択しても勿論良い。

(d) フィルタ1を構成する場合、セラミック部材2、3相互間にヒータを設けてなる構成としてもよい。この場合、ヒータは金属線であることのみに限定されない。つまり、ヒータは、金属メタライズ、導体ペーストの印刷、スパッタリング等といった方法によって作製したものであってもよい。

10 【0044】本実施例においては、この発明のセラミック構造体を、ディーゼルエンジンに取り付けられる排気ガス浄化装置用フィルタに具体化した例について説明したが、このセラミック構造体は、排気ガス浄化装置用フィルタ以外にも、例えば、熱交換器用部材、あるいは高温流体、高温蒸気の濾過フィルタとして使用することができる。

【0045】

【発明の効果】以上説明したようにこの発明のセラミック構造体は、温度に関係なく接着強度に優れ、しかも熱伝導率にも優れるので、例えば、排気ガス浄化装置用フィルタに適用すると、再生時間の短縮、再生効率や耐久性の向上を実現することができる。

【図面の簡単な説明】

【図1】この発明のセラミック構造体を用いた排気ガス浄化装置用フィルタを示す斜視図である。

【図2】この発明のセラミック構造体を用いた排気ガス浄化装置用フィルタの部分拡大断面図である。

【図3】この発明にかかる排気ガス浄化装置用フィルタのセラミック部材を示す斜視図である。

30 【図4】図3のA-A線における一部破断拡大断面図である。

【図5】図4のB-B線における拡大断面図である。

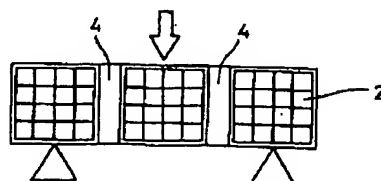
【図6】接着強度の測定試験の説明図である。

【図7】熱伝導率の測定試験の説明図である。

【符号の説明】

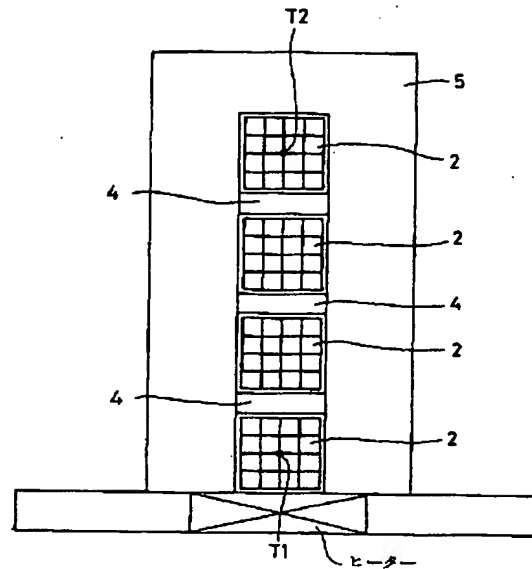
- 1 排気ガス浄化装置用フィルタ
- 2, 3 セラミック部材
- 4 シール材
- 5 断熱材

【図6】



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【図 7】



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